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Polymer 44 (2003) 79–88

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Exotherm control in the thermal polymerization of nona-ethylene glycol dimethacrylate (NEGDM) using a dual radical initiator system

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Received 14 February 2002; received in revised form 8 October 2002; accepted 16 October 2002

Abstract

The curing behaviour of a long-chain dimethacrylate with a series of peroxide initiators was examined by temperature-ramping DSC. The effect of oxygen inhibition on the onset and peak temperatures cure was confirmed and the peak exotherm temperature was correlated with the decomposition rate of the initiator. The gel point temperature, obtained from temperature-ramping rheology studies, was directly related to the onset of cure from temperature-ramping DSC measurements. A combination of two peroxides with significantly different initiation rates was found to reduce the maximum heat flow and spread the polymerization process over a broader range of temperatures, thus effectively counteracting the auto-acceleration effect without significantly affecting the degree of cure. This behaviour was also predicted by with a free radical polymerization kinetic model. In order to further improve the cure behaviour, Nofmer was used as a chain transfer agent to control the propagation reaction in the polymerization. The use of a dual initiator system in the presence of Nofmer yielded a smooth polymerization process occurring over a wide range of temperatures and with low heat flow. Isothermal rheological studies confirmed the delay in the gel point by Nofmer.

Keywords: Dimethacrylate cure; DSC; Chemorheology; Dual/mixed initiators; Chain transfer agent

1. Introduction

The Trommsdorff or gel effect [1] in the free radical polymerization of acrylic systems has been of industrial and scientific interest for many years. The auto-acceleration of the reaction is generally attributed to the decreased diffusion rate of the chain radicals due to the increased viscosity of the mixture, which reduces the termination rate and thus raises the polymerization rate [1,2]. In addition to the auto-acceleration of the reaction, the exothermic nature of the polymerization can cause excessive heat generation [3], resulting in premature gelation or the production of polymer with residual stresses, birefringence, or voids. A more serious risk is an uncontrolled runaway reaction and avoidance of this danger restrains production efficiency for the manufacture of acrylic polymers—casting methacrylates to produce sheets, rods and molding compounds usually requires very long curing cycles, which is economically disadvantageous [4].

An appropriate selection of the initiator [4–10] or use of a chain transfer agent [11,12] can often successfully control the polymerization exotherm. The mechanism by which an initiator or a chain transfer agent affects the exotherm is however different. As the first step in a free radical chain polymerization, the initiation process is largely dependant upon the structural nature of the initiator [2] and the curing conditions, particularly the curing temperature. Since each initiator has a specific decomposition rate at a given temperature, the matching of the characteristics of initiator and its concentration with the curing conditions is of great significance for obtaining a smooth cure. In fact, the technique of using a combination of different initiators has been found capable of providing rapid but controlled polymerization with low residual monomer content [5–10]. However, in a study of styrene polymerization initiated by a dual initiator system of *t*-butyl perbenzoate and benzoyl peroxide, Kim et al. [13–15] found that, although the use of a binary initiator mixture can give an additional degree of freedom to reactor operators, the presence of the second initiator species significantly increases the complexity of the reactor dynamics. Chain

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0032-3861/03/$ - see front matter © 2002 Published by Elsevier Science Ltd.
PII: S0032-3861(02)00766-8

transfer agents, on the other hand, are widely used in both industrial and scientific research to control the molecular weight of polymers [1] as well as the polymerization rate [11,12] by controlling the kinetic chain length and thus the Trommsdorff effect.

In the present paper, we investigate a series of organic peroxides as initiators for the bulk polymerization of nona(ethylene glycol) dimethacrylate (NEGDM) and report on studies of the kinetics of thermal polymerization of NEGDM used a dual initiator system, based on a mixture of either bis(4-*t*-butylcyclohexyl) peroxy dicarbonate (BCHP) or *t*-butyl peroxy-2-ethylhexanoate (TBPEH) with 2,5-dimethyl hexane-2,5-di(*t*-butyl peroxide) (DHBP). The effect of the chain transfer agent, α-methylsytrene dimer, on the polymerization kinetics and the control of polymerizatfion exotherm of NEGDM with TBPEB/DHBP are also studied. These results are correlated with the rheological changes during cure.

2. Experimental

Nona(ethylene glycol) dimethacrylate (NEGDM—see Fig. 1), purchased from Shin-Nakamura Chem. Co. (Japan), was used without further purification. Previous studies [16] of a commercial sample of NEGDM found it to be polydisperse and to consist of oligo(ethylene-oxide) dimethacrylates with 3–14 ethylene oxide units—the polydispersity of the current resin has been confirmed by GPC [17]. The resin was degassed in vacuum prior to polymerization. As shown in Fig. 2, a series of organic peroxides, ranging from a peroxy dicarbonate (BCHPC), a diacyl peroxide (BPO), two peresters (TBPEH and TBPB) and two dialkyl peroxides (DCP and DHBP) with different decomposition rates were used as thermal initiators for the bulk polymerization of NEGDM—their characteristic temperature for a half-life of 1 min, 1 h and 10 h are summarized in Table 1 [18]. These values are very close to those given by Moad [19] and other workers [3,20]. The standard concentration of the initiators in NEGDM was 1 wt% except for BCHPC, which was used at 0.34 wt% due to its limited solubility in the monomer. Mixtures of varying ratios of BCHPC/DHBP and TBPEH/DHBP were also used. In order to control the gel effect in the polymerization, the effect of a chain transfer agent, 2,4-diphenyl-4-methyl-1-pentene (Nofmer MSD, Nofmer Corporation—Fig. 1) on the cure kinetics was also investigated.

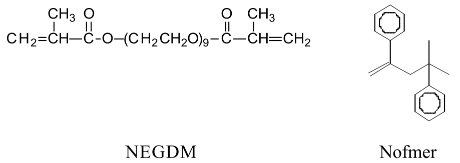
NEGDM Nofmer

Fig. 1. Molecular structures of NEGDM and Nofmer chain transfer agent.

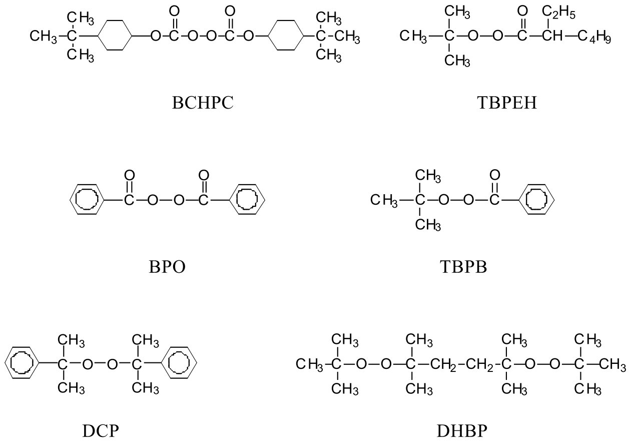
BCHPC TBPEH BPO TBPB DCP DHBP

Fig. 2. Molecular structures of peroxide initiators.

A Perkin–Elmer DSC-7 calorimeter was used to study the polymerization kinetics during temperature-ramping cure experiments. The DSC was calibrated using indium and zinc standards and a heating rate of 10 °C/min was used. The resin samples were sealed in sample pans under nitrogen, or when specified, under an air atmosphere to investigate the effect of oxygen on the polymerization, prior to study.

Rheological changes during the polymerization were monitored under temperature-ramping conditions with a typical temperature range of 30–200 °C and a scan rate of 5 °C/min, by measurements of the steady shear viscosity at a nominal shear rate of 1 s^{-1} with a Bohlin CS-50 Rheometer, using a parallel plate (40 mm in diameter) with a gap of 0.5 mm which gives a stress range of 0.06–3000 Pa. The samples were degassed before the measurement but no nitrogen blanket was applied during the rheology experiments. Duplicated rheology studies showed that although the absolute viscosity values varied from run to run (especially at high viscosities), the shape of the viscosity traces were the same. Because the viscosity diverges to infinity during gelation [21,22], the gel point temperature was defined as the point where the viscosity started to rise abruptly.

Isothermal rheology experiments were also performed at temperatures of 50–80 °C, by measuring the dynamic shear moduli (G' and G'') at 1 Hz using the instrument set-up described above but with strains varying from 1 (at the start of the measurement) to 0.05 (when the material had gelled). The samples were degassed before the measurement but no nitrogen blanket was applied during the experiments. Because the real modulus rises rapidly near the gel point [22], gelation was operationally defined as the time where the real modulus rose abruptly. Some isothermal steady shear viscosity studies of the curing process were also undertaken. While the gel times measured in the dynamic experiment correlated well with the steady shear method, the dynamic method was preferred for the lengthy, isothermal rheology experiments because the small dynamic strain applied did not cause as much disturbance of the

Table 1
A summary of initiator half-life temperatures [18]

Code	Chemical name	Half-life temperature (°C)			Physical form	Supplier
		10 h	1 h	1 min		
BCHPC	Bis(4-*t*-butylcyclohexyl) peroxy dicarbonate	41	58	92	Powder	Akzo Nobel
BPO	Dibenzoyl peroxide	74	92	130	Powder	Aldrich
TBPEH	*t*-Butyl peroxy-2-ethylhexanoate	72	92	134	Liquid	Interox
TBPB	*t*-Butyl perbenzoate	104	125	167	Liquid	Interox
DCP	Dicumyl peroxide	116	136	175	Powder	Aldrich
DHBP	2,5-Dimethyl hexane 2,5-di-*t*-butyl peroxide	118	138	180	Liquid	Interox

sample which minimized the mixing of the sample with atmospheric oxygen, thus reducing inhibition effects.

3. Results and discussion

3.1. DSC investigation of oxygen inhibition

The effect of oxygen inhibition on free radical polymerization is well known [1]. Oxygen is an efficient scavenger of both initiating and propagating species in radical polymerization and this process is usually extremely fast. The rate constants for quenching carbon-centred radicals by oxygen molecules, for example, generally exceed $10^9\ \mathrm{M}^{-1}\mathrm{s}^{-1}$, which is at the diffusion limit [23,24]. As a result, the presence of oxygen in the radical polymerization of coatings and composites often causes serious problems, including low cure rate and cure conversion, which render the products tacky and with poor mechanical properties and durability [25].

DSC was used to study the oxygen inhibition effect on the polymerization of NEGDM initiated by 1 wt% BPO or TBPEH. The DSC heat flow [26,27], which is proportional to the polymerization rate, can be used to study the polymerization kinetics and the onset temperature (T_{onset}) and peak temperature (T_{p}) are often used as guides for choosing cure conditions. The thermograms during the polymerization of NEGDM in nitrogen and in air are shown in Fig. 3. The effect of oxygen inhibition on the polymerization of NEGDM is clearly shown by the shift of the peak to higher temperatures for the NEGDM resin sealed in an air atmosphere (see also Table 2). An integration of the DSC peaks provides the heat of polymerization for NEGDM of 229 J/g or 126 kJ/mol (based on the idealized structure in Fig. 1). This value is close to the estimated heat of polymerization for NEGDM (119 kJ/mol), based on the polymerization heat [4] of butylmethacrylate (59.4 kJ/mol).

Table 2
The heat of polymerization and onset and peak temperatures of DSC thermogram for NEGDM polymerization in the atmosphere of nitrogen and air

Atmosphere	N_2		Air	
Initiator (1 wt%)	TBPEH	BPO	TBPEH	BPO
T_{onset} (°C)	87	85	90	93
T_{p} (°C)	91	93	95	99
ΔH (J/g)	233	227	239	218

3.2. Activation energy

Although the activation energy for a polymerization can be obtained from an analysis of one single dynamic DSC scan, such as is employed by commercial software, this technique is successful only for some reactions and in particular first order reactions [27]. An alternative technique capitalizes on the variation in peak exotherm temperature with DSC heating rate [27–29] and gives a relatively accurate measure of the activation energy (E_{a}) for all reaction orders. Fig. 4 shows an example of the calorimetric analysis of NEGDM polymerization under nitrogen with BPO as the initiator using different DSC scan rates (Φ). The Kissinger [28] analysis relates the activation energy (E_{a}) to the DSC heating rate Φ and T_{p} by the following equation

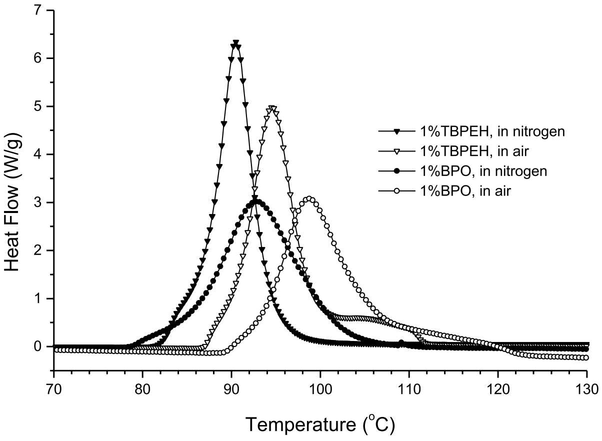

Fig. 3. Normalized DSC curves for polymerization of NEGDM in nitrogen and air.

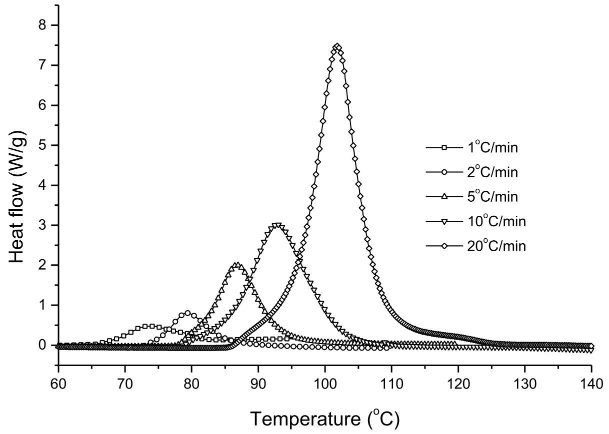

Fig. 4. DSC thermograms under different scan rates for the polymerization of NEGDM initiated by 1 wt% BPO.

[27,28]:

$$\ln\left(\frac{\Phi}{T_p^2}\right) = -E_a/RT_p + \ln\left(\frac{AR}{E_a}\right) \quad (1)$$

where A is the pre-exponential factor.

A linear regression of the plot of $\ln(\Phi/T_p^2)$ against $1/T_p$ gave the activation energies for the polymerization of NEGDM with BPO, in air and nitrogen of 122 ± 10 and 113 ± 6 kJ/mol, respectively. A comparable activation energy (125 ± 14 kJ/mol) was found when the polymerization was initiated by TBPEH under N_2, which is in accord with the similarity of their activation energies for decomposition [18].

3.3. Comparison of peroxide initiators

A careful selection of the initiator for the chosen curing temperature is required in order to obtain controlled polymerization. The most important characteristic of the initiator is its decomposition rate, often expressed by its half-life ($t_{1/2}$) or its half-life temperature. Fig. 5 shows the DSC thermograms for NEGDM sealed under N_2 and initiated by several peroxides with differing half-life temperatures (see Table 1). In general, single exotherms were observed however, the broad exothermic peak for DHBP-initiated polymerization in Fig. 5 may be a combination of several sub-peaks, arising from multiple stages in the decomposition of the initiator, as suggested by Moad [19]. The heat of polymerization does not significantly vary with the initiator type, suggesting that the extent of cure and the final network structure is independent of the polymerization rate. Among the peroxides studied, BCHPC is the least stable initiator and hence initiates the polymerization at the lowest temperature, whereas DHBP is the most stable initiator and gives the highest initiation temperature. Fig. 6 shows that there exists a strong (almost 1:1) relationship between the DSC peak temperature and the initiator half-life temperature. Such a simple relationship is perhaps surprising, however since the half-life temperature is the temperature at which the initiator has decomposed to a certain level (50%) it should be strongly correlated with the rate of polymerization and thus the peak exotherm temperature. It should be noted that although the peroxides vary considerably in type (peroxy dicarbonate, diacyl peroxide, perester and dialkyl peroxide—see Fig. 2) and will thus form a range of radical species including methyl, phenyl and alkoxy [2,19], this should not directly affect the propagation rate (since many propagation steps result from one initiation step) but should only affect the initiator efficiency through the occurrence of side reactions.

Fig. 7 illustrates the variation in steady shear viscosity of NEGDM with different initiators during temperature ramping cure (5 °C/min). Initially, the viscosity has a low constant value but as the temperature is raised it abruptly rises due to the commencement of polymerization followed by gelation and the development of a crosslinked network system. Gelation can only occur after sufficient free radicals have been formed and have consumed all inhibitors (e.g. stabilizer and oxygen) so that the polymerization reaction

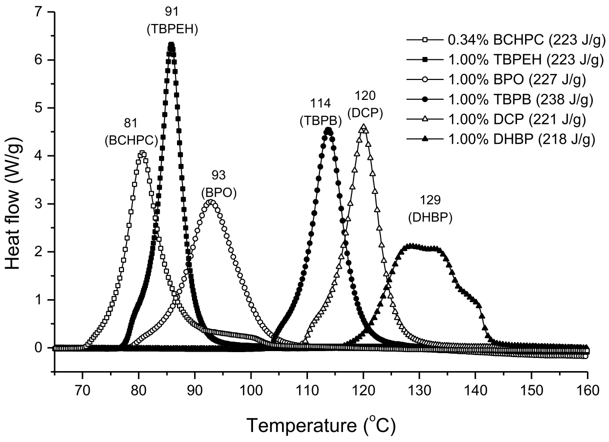

Fig. 5. DSC profile for NEGDM polymerization using different peroxide initiators.

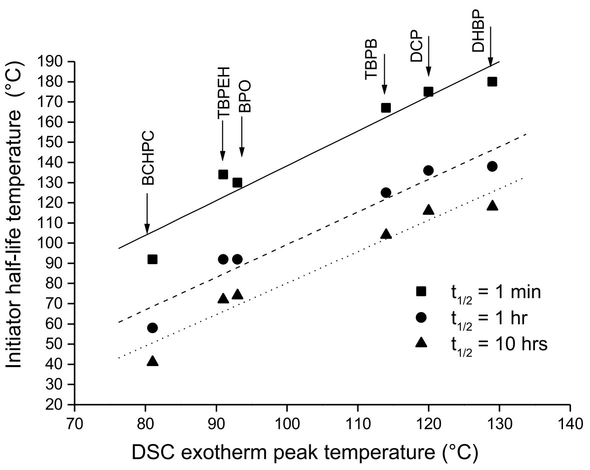

Fig. 6. Relationship of the half-life temperatures of peroxide initiators and their DSC peak temperatures in the polymerization of NEGDM. The lines are least-square fits to the data.

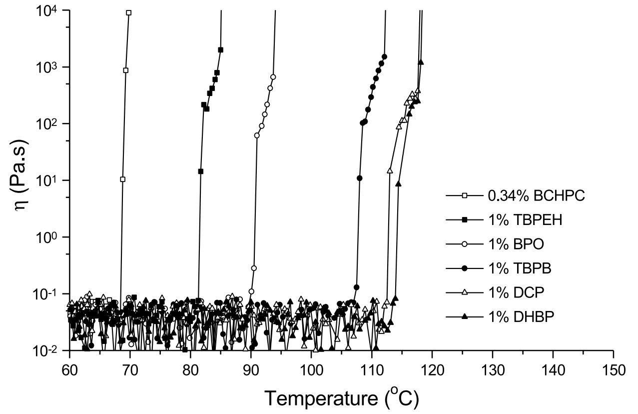

Fig. 7. Variation in steady shear viscosity during NEGDM polymerization initiated by different peroxide initiators (temperature ramping rate: 5 °C/min).

can proceed to produce a three-dimensional structure [1]. Thus, the gel point temperature is strongly dependent on the initiator stability, with the result that gelation will take place at a higher temperature when the initiator has an elevated decomposition temperature. Since the gel point for divinyl monomers is not more than several percent [30], the onset of polymerization in a temperature ramping DSC trace should correspond closely to the gel point. Therefore, the DSC onset temperature should be close to the gel point temperature. Taking into account the difference in heating rate used in the DSC and rheology experiments, a good 1:1 correlation is seen in Fig. 8. A similar correlation was also observed between the gel point temperature and the DSC peak temperature but the latter was higher than the former.

3.4. Investigation of dual initiator polymerization

A common problem with non-isothermal polymerization of a vinyl monomer with a thermally activated initiator is the gel effect, which leads to rapid increase in polymerization rate [1] and, under non-isothermal conditions, a rise in temperature which has the feed-back effect of accelerating the rate of initiator decomposition. This can lead to severe exotherms [1,3] but in other cases this acceleration of the initiator decomposition may lead to 'dead-end polymerization' [31], where the total depletion of initiator occurs before polymerization is complete. A possible way to overcome these problems is to use two initiators with significantly different decomposition rates. Two initiator pairs (BCHPC/DHBP and TBPEH/DHBP) were evaluated as the mixed initiator system for the polymerization of NEGDM.

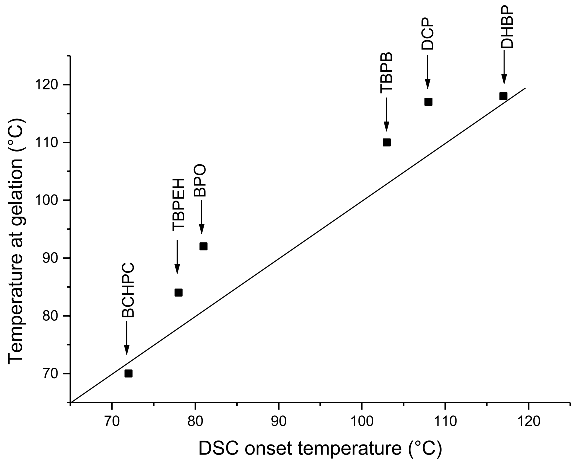

Fig. 8. Comparison of the DSC onset temperature with gel point temperature during temperature ramping cure for NEGDM cured by 1 wt% of various initiators. The line represents a one-to-one correlation.

The polymerization profiles produced by the BCHPC and DHBP initiator pair are shown in Fig. 9. The heat of polymerization was approximately independent of the initiator formulation and had an average of 220 J/g which is close to that reported above. At most initiator ratios, the initiation process was predominantly controlled by BCHPC, that is, the initiator with lower stability. When the BCHPC/DHBP ratio was reduced (with the total concentration of initiators being maintained at 1 wt%), the peak temperature increased due the decrease in polymerization rate. However, even at a low levels of BCHPC (e.g. 250 ppm) in the dual initiator system, the polymerization occurred in a much lower temperature range and the rate maximum was lower than that found using DHBP as a single initiator. In most cases, two separate peaks, or a major peak with a shoulder, were observed in thermograms due to the decomposition of BCHPC (at low temperatures) and of DHBP (at high temperatures).

BCHPC is a solid and has a limited solubility in the monomer, which hampers its application as an initiator for NEGDM. The low temperature initiator, TBPEH, on the other hand, is a liquid and can be conveniently mixed into common acrylic monomers for the preparation of curable formulations. Therefore, the mixture TBPEH and DHBP was also investigated as the dual initiator system for the polymerization. Similar to the BCHPC/DHBP combination, the dual initiator system of TBPEH/DHBP in the NEGDM polymerization gave an average heat of polymerization of

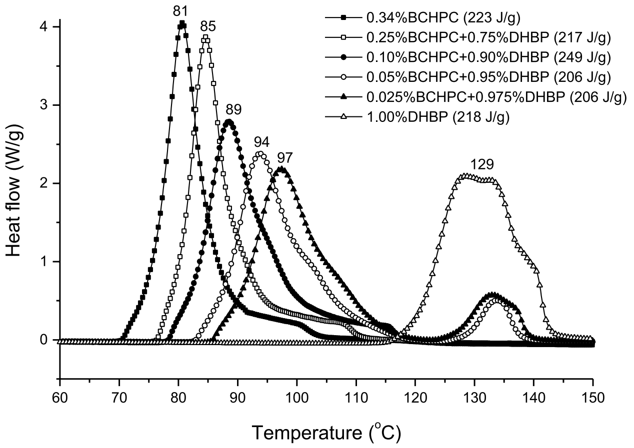

Fig. 9. Polymerization of NEGDM initiated by the dual initiator system: BCHPC/DHBP.

236 J/g. The mixed initiator system also reduced the maximum polymerization heat flow, broadened the exothermic process and raised the peak temperature as the TBPEH:DHBP ratio was lowered, as shown by the DSC thermograms in Fig. 10. The suppressed polymerization rate and the broadened exothermic peak at very low levels of TBPEH amount (particularly for levels less than 0.1 wt%), suggest an improved control of the polymerization kinetics and reaction exotherm under non-isothermal cure conditions.

The variation in viscosity during the NEGDM polymerization using the dual initiator system (TBPEH/DHBP) was studied under temperature ramping conditions (5 °C/min) and the data are shown in Fig. 11. As discussed above, the onset temperature for gelation indicates the point where a small amount of polymerization has occurred and so should be related to the cure kinetics. As was found for single initiator systems (see Fig. 8), a good correlation is observed between the gelation temperature and the DSC onset temperature (see Fig. 12)—a related correlation was also observed for the DSC peak temperature and the gel temperature.

3.5. DSC simulation

In an earlier paper [16], one of the authors developed a chemico-diffusion model for predicting the rate of polymerization of a divinyl monomer. This model was used as a basis for simulating the DSC results shown in Figs. 9 and 10. Assuming that the steady state approximation is valid, the rate of conversion can be given by [1]:

$$d\alpha/dt = [(k_p^2/k_t)(g_1 f_1 k_{d1}[I_1] + g_2 f_2 k_{d2}[I_2])]^{1/2}(1-\alpha) \qquad (2)$$

where k_p and k_t are the propagation and termination constants, α is the conversion and k_{di} and $[I_i]$ are the decomposition rate constant and concentration of initiator I_i and g_i is the number of radicals generated per decomposing initiator and f_i is the initiator efficiency. For simplicity, all initiator radicals were assumed to have the same activity.

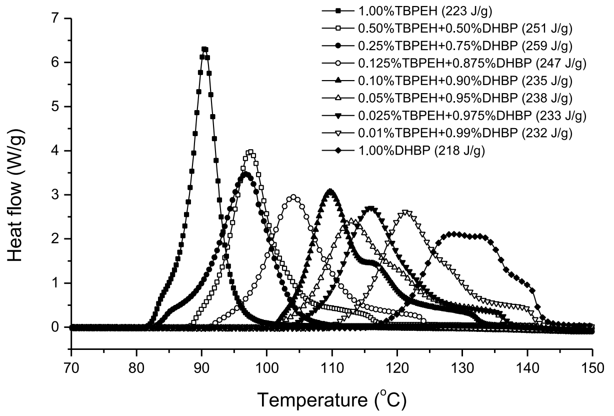

Fig. 10. Polymerization of NEGDM initiated by the dual initiator system: TBPEH/DHBP.

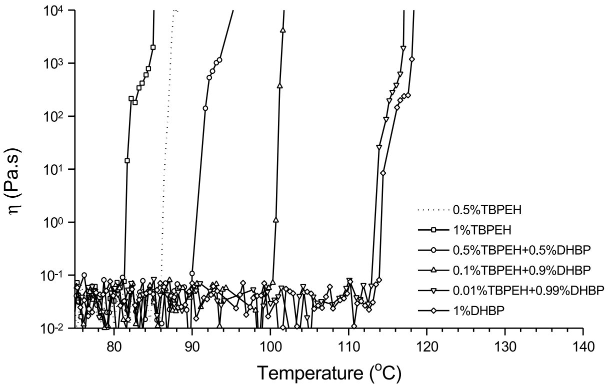

Fig. 11. Variation in steady shear viscosity during the NEGDM polymerization initiated by a dual initiator system of TBPEH/DHBP under temperature ramping (5 °C/min).

The rate constant for initiator decomposition is given by [1]:

$$k_{di} = A_{di}\exp(-E_{di}/RT) \qquad (3)$$

where A_{di} and E_{di} are the collision parameter and activation energy, respectively, and were calculated from the half-lives given in Table 1.

A diffusion dependency of the propagation and termination rate constants was incorporated in the model [16] but differences in reactivity of monomer and pendant vinyl groups was ignored. Since propagation requires a diffusional step followed by a collision step, the propagation rate constant can be written as [16]:

$$k_p = \frac{1}{\dfrac{1}{k_{p(\mathrm{chem})}} + \dfrac{1}{k_{p(\mathrm{diff})}}} \qquad (4)$$

where the chemical rate constant ($k_{p(\mathrm{chem})}$) is given by the Arrhenius expression [1]:

$$k_p = A_p\exp(-E_p/RT) \qquad (5)$$

and the diffusional rate constant ($k_{p(\mathrm{diff})}$) is given by a

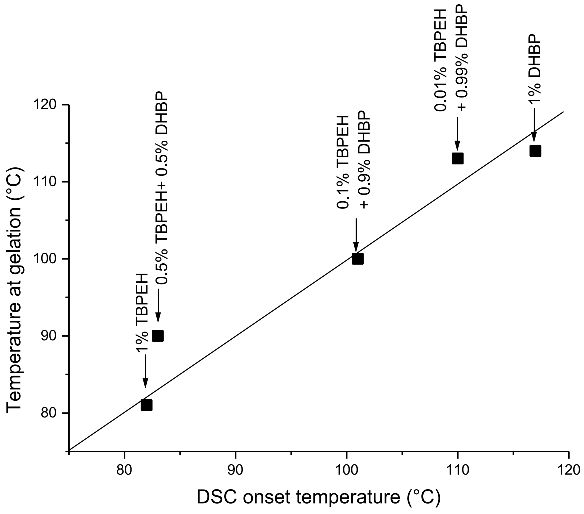

Fig. 12. A comparison of DSC onset temperature with gel point temperature during temperature scanning. The line represents a one-to-one correlation.

WLF-like expression [16]:

$$k_{p(\text{diff})} = k_{\text{diff}(T\text{g})} \exp\left[\frac{c_1(T - T_g)}{c_2 + T - T_g}\right] \quad (6)$$

where T_g is the glass transition temperature, $k_{\text{diff}(T\text{g})}$ is the monomer diffusion rate constant at T_g and c_1 and c_2 (assumed to be 40 and 50 °C, respectively, [32]) are the WLF constants. For simplicity, the T_g was assumed to be a linear function of the conversion between the monomer (assumed to be −50 °C which is close to that found for other related monomers [16]) and the NEGDM network [16,33] (25 °C).

Since termination can occur by either diffusion of the chain segments (translational/segmental diffusion [2]) or by propagation of one chain towards another (reaction diffusion [2]), the termination rate constant combined a translational/segmental diffusion term ($k_{t(\text{trans/seg})}$) with a reaction diffusion term ($k_{t(\text{react})}$) [16]:

$$k_t = k_{t(\text{trans/seg})} + k_{t(\text{react})} \quad (7)$$

Following the analysis in the earlier paper [16], these two terms were written in the form:

$$k_{t(\text{trans/seg})} = \exp(-20\alpha)k'_{\text{diff}(T\text{g})} \exp\left[\frac{c_1(T - T_g)}{c_2 + T - T_g}\right] \quad (8)$$

$$k_{t(\text{react})} = k'k_p(1 - \alpha)[\text{M}]_0 \quad (9)$$

where $[\text{M}]_0$ is the monomer concentration and the first exponential term in Eq. (8) was used to simulate the drop in k_t with conversion due to steric hindrance to translational/segmental radial diffusion.

Previously [16], the initiator efficiency was calculated from the rate constant for radical recombination and from the rate of small molecule diffusion (i.e. radical separation from the cage) and no allowance was made for side reactions of the initiator radical. Given that the two initiators could have differing efficiencies, for simplicity, in the present work, f was set at a value of 0.2, which is a typical value in a semi-viscous medium [2]. Table 2 lists the values of the parameters used in the DSC simulation.

Using the temperature ramping conditions of 5 °C/min from 30 °C till complete cure, Eq. (2) was solved by an iterative process. After setting the initial values for the model parameters, the time was incremented by 2 s and the corresponding temperature, initiator decomposition rates, initiator concentrations, T_g, polymerization rate constants (k_p, k_t), conversion rate and conversion were calculated. The time was successively incremented and the parameters re-evaluated until the polymerization was complete. Simulations with either twofold larger or smaller time steps did not significantly affect the results.

Fig. 13 shows the predicted variation in conversion rate ($d\alpha/dt$) at a scanning rate of 5 °C/min for NEGDM initiated with mixtures of BCHPC and DHBP. For the NEGDM/BCHPC system, the calculated polymerization rate curve (Fig. 12) is similar to the corresponding DSC curve (Fig. 9) but has a peak at a lower temperature. For the DHBP system, the simulation predicts a slightly sharper peak (due to the higher activation energy for decomposition of this initiator—see Table 3) and is unable to model the observed DSC shoulders. As discussed by Moad [19] and mentioned above, this may be due to the multi-stage decomposition of the initiator to form initiator radicals. When mixtures of the two initiators are used, the predicted rate curve broadens and exhibits two peaks as found in the DSC thermograms however it was not possible to attain a perfect match by adjustment of the initiator efficiency. A related correlation was found between the experimental heat flow curves and the predicted cure behaviour of NEGDM with mixtures of TBPEH and DHBP however in these cases a much lower value (ca. 0.01) of initiator efficiency was required to attain an optimum correlation. Thus the model confirms that mixtures of initiators should produce double-peaked and broadened DSC curing curves but quantitative agreement between simulation and experiment was not found. This failure is perhaps due to limitations in the chemico-diffusional modeling [16] or because of multi-stage initiator decomposition or is a result of interactions between initiator radical fragments.

3.6. Effect of chain transfer agent on the polymerization

In order to improve the control of the polymerization exotherm, the effect of the chain transfer agent, 2,4-diphenyl-4-methyl-1-pentene (Nofmer), was investigated. Fig. 14 reveals that Nofmer exerts a significant retarding effect on the NEGDM polymerization because it delays gelation and thus the Trommsdorff effect [1,2]. With an increase in the amount of chain transfer agent, the maximum heat flow was reduced and the peak temperature was raised, as was breadth of the exotherm peak, however, Nofmer did not affect the cure conversion as shown by the constant values for the reaction enthalpy.

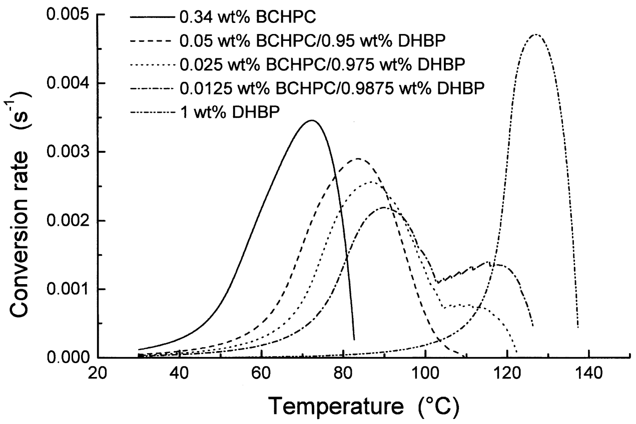

Fig. 13. Predicted conversion rate of NEGDM with varying amounts of BCHPC and DHBP during temperature ramping (5 °C/min).

Table 3
Values of parameters used in the DSC simulation

Parameter[a]	Value
A_p	$6 \times 10^6\ M^{-1}s^{-1}$
E_p	25 kJ/mol
$k_{diff(Tg)}$	$10^{-3}\ M^{-1}s^{-1}$
$k'_{diff(Tg)}$	$10^{-7}\ M^{-1}s^{-1}$
$k'\ [M]_0$	100
f	0.2
A_{d1} (BCHPC)	$1.5 \times 10^{15}\ s^{-1}$
E_{d1} (BCHPC)	120 kJ/mol
g_1 (BCHPC)	2
A_{d1} (DHBP)	$3.7 \times 10^{15}\ s^{-1}$
E_{d2} (DHBP)	152 kJ/mol
g_1 (DHBP)	4

[a] With the exception of f all polymerization kinetics parameters were taken from Ref. [16]. The initiator decomposition were determined from the data in Ref. [18].

Fig. 15 illustrates the evolution of the real shear modulus (G') during isothermal cure of NEGDM with TBPEH at different temperatures and in the presence of Nofmer. The real shear modulus was initially low due to the liquid state of the material but when gelation occurred, the shear modulus increased by five orders of magnitude within a short period of time and then approached a plateau. The plateau modulus of approximately 10^6 Pa suggests a rubbery state at the test temperatures, in agreement with previously reported DMTA data [33] that showed the glass transition temperature for the fully cured NEGDM polymer to be 25 °C. Raising the polymerization temperature reduced the time for the gelation to occur due to the increase in the reaction rate. If gelation is considered to occur at a constant low conversion level, then the gel time can be taken as being inversely related to the rate of the polymerization process [34,35]. Thus, a logarithmic plot of gel time (t_{gel}) versus reciprocal temperature (Fig. 16) yielded an activation energy of 141 ± 4 kJ/mol for the initiation of the curing process which was close to the activation energy obtained by the Kissinger method [28] (125 ± 14 kJ/mol). It should be born in mind that the activation energy for gelation is primarily associated with the consumption of the inhibitor during the decomposition of the initiator and as a result, it compares reasonably well with the activation energy for TBPEH decomposition (120 kJ/mol [18]). The retardation of the gel effect by Nofmer during the polymerization is also clearly evidenced by the rheological behaviour shown in Fig. 15—Nofmer delayed the gelation approximately in proportion to the amount of the chain transfer agent used.

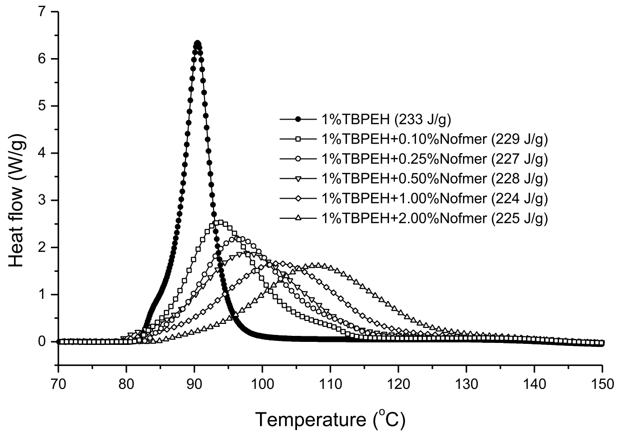

Fig. 14. DSC thermograms (10 °C/min) for NEGDM polymerization initiated by 1 wt%TBPEH in the presence of Nofmer.

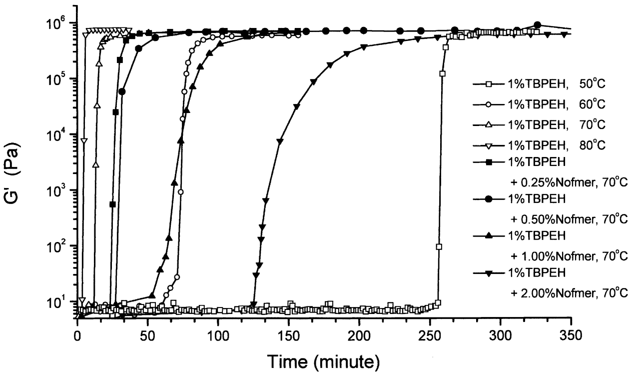

Fig. 15. Dynamic real modulus with time showing the effect of Nofmer as a chain transfer agent on the isothermal polymerization of NEGDM initiated by 1 wt% TBPEH.

3.7. DSC study of NEGDM polymerization with a dual initiator and a chain transfer agent

Temperature-ramping DSC was used to study the polymerization of NEGDM initiated by the dual initiator system, TBPEH/DHBP, in the presence of Nofmer chain transfer agent. The thermograms depicted in Fig. 17 show that the addition of the chain transfer agent reduces the peak heat flow and extends the exothermic process over a wider temperature range than that produced by the TBPEH/DHBP dual initiator system alone. Similar to that reported above, when the mixed catalyst system was used in conjunction

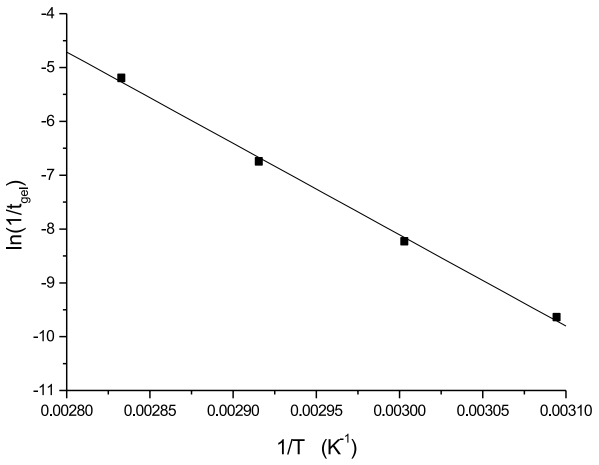

Fig. 16. Temperature dependence of gel point (t_{gel}) for the isothermal polymerization of NEGDM initiated by 1 wt% TBPEH.

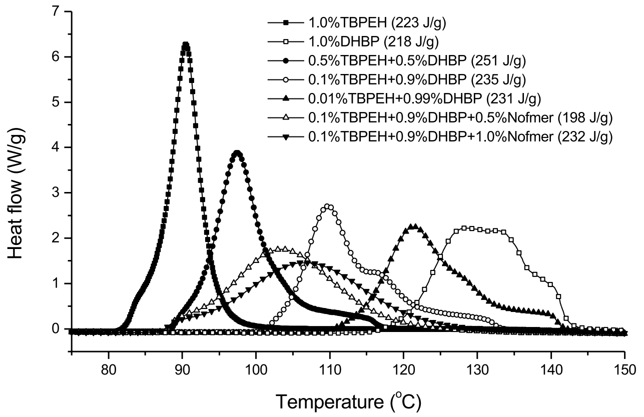

Fig. 17. DSC thermograms for the NEGDM polymerization initiated by a dual initiator system (TBPEH/DHBP) in the presence of Nofmer.

with Nofmer, the heat of polymerization was virtually unaffected and 'full cure' was observed. Hence, the combined use of dual initiator and chain transfer agent could potentially provide a solution to reducing the Trommsdorff effect in the polymerization of acrylic systems and consequently allow regulated polymerization with improved cure characteristics.

4. Conclusions

The thermal polymerization of NEGDM was investigated using a series of peroxide initiators: BCHPC, TBPEH, BPO, TBPB, DCP and DHBP. The cure behaviour was studied by temperature-ramping DSC experiments in air and N_2 and the effect of oxygen inhibition was confirmed. The activation energy at the maximum rate was determined by temperature-ramping DSC studies and was similar to the activation energy determined from the isothermal gel time. A strong correlation was observed between the peak temperature in the temperature ramping DSC and the initiator half-life temperatures. Good agreement was found between the DSC onset cure temperature and the gel point temperature determined by temperature-ramping rheology measurements because gelation occurred shortly after the commencement of polymerization.

The use of mixtures of two peroxides with significantly different half-life temperatures was found to produce two exotherm peaks and to spread the polymerization over a wider temperature range in the temperature-ramping DSC experiment. This reduced the maximum polymerization rate, thus potentially suppressing thermal over-runs and temperature gradients during non-isothermal curing. Simulation of these temperature-ramping DSC experiments also predicted double peaks and a broadening of the cure process over a wider temperature range. In order to further improve the polymerization kinetics, the chain transfer agent, Nofmer, was used to control the polymerization rate. Scanning DSC showed that Nofmer retarded the polymerization and broadened the temperature range of the exotherm because it delayed the gel point and thus reduced the Trommsdorff effect. These conclusions were confirmed by isothermal rheology studies, which confirmed that Nofmer retarded the gel point. Thus the application of a dual initiator system (TBPEH/DHBP) in conjunction with Nofmer appears to produce a more smoothly controlled polymerization with a lower peak rate.

Acknowledgements

The authors gratefully acknowledge the financial and technical support from the Cooperative Research Centre for Polymers and the helpful discussions with Drs Huan Toh, David Lewis, Richard Evans, David Morsley, Jason Watling, Graeme Moad and Professor Tom Davis.

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